

# Investigation by Two-Dimensional NMR of the Structure and Stereochemistry of a Methyl *p*-Nitrocinnamate Photodimer

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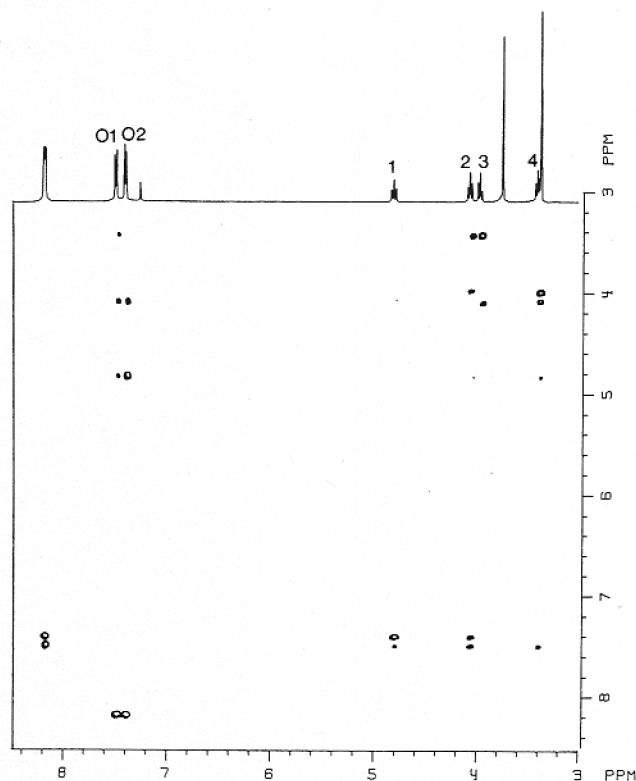
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Current research in our laboratory (BG) is directed toward controlling the stereo- and regiochemistry of photochemical dimerizations. This prompted us to reinvestigate the products reported by Ishigami et al.<sup>1</sup> to be formed from the irradiation of (*E*)-methyl *p*-nitrocinnamate, **1**, in solution. In addition to two head-to-head dimers these authors isolated material, in low yield, which was stated to be a mixture of two head-to-tail dimers. As we had chosen to try to control the stereochemical course of this photodimerization, and as there was a continuing interest in assigning the structure and stereochemistry of photodimers, we reexamined the presumed mixture of head-to-tail dimers.

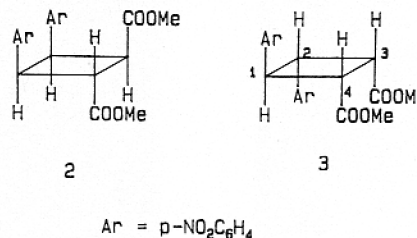
Ishigami et al. did not separate the mixture of head-to-tail dimers and appear to have based their structural assignment on the assumption that the photoproducts were derived solely from the methyl *E* isomer. In the absence of other evidence, the complex absorption of the cyclobutane protons at 60 Mz and the presence of two carbomethoxy resonances were consistent with their assignment. We have repeated the irradiation as described and recorded the NMR spectrum of the reported mixture at 200 and 500 MHz. At the higher fields we were able to separate the cyclobutane resonances as triplets of equal area centered at 4.81 (H-1), 4.05 (H-2), 3.99 (H-3), and 3.43 ppm (H-4). Signals from the carbomethoxy groups appear at 3.75 and 3.38 ppm and were also of equal area. Thus, the material could be a 1:1 mixture as suggested by Ishigami or a single compound that lacked the usual symmetry present in photodimers. This question was effectively settled by a COSY spectrum (included in supplementary material) which shows that each cyclobutane proton is coupled to two others, H-1 to H-2 and H-4 and H-3 to H-2 and H-4. This observation requires that these signals arise from a single compound. Further, the absence of cross peaks between H-1 and H-3 as well as between H-2 and H-4 shows that H-1 and H-3 are situated at opposite corners of the cyclobutane, as are H-2 and H-4.

Ishigami et al. noted,<sup>1,2</sup> and we have confirmed, that in addition to photodimerization, extensive *E* to *Z* isomerization occurs during the irradiation of **1**. As substantial quantities of the *Z* isomer were present in solution it appeared possible that the minor photoproducts could be derived from photoaddition reactions involving this isomer.



**Figure 1.** Absorption mode 2D NOE spectrum of **3**. The spectrum results from a  $2 \times 400 \times 1024$  data matrix, i.e., per  $t_1$  value two sets of 1024 data points each, corresponding to odd and even numbered scans, are stored separately.<sup>5</sup> A mixing time of 900 ms was used, slightly shorter than the average  $T_1$  value of the cyclobutane ring protons. Data acquisition times were 80 and 102 ms in the  $t_1$  and  $t_2$  dimension, respectively. Sixteen scans were recorded per  $t_1$  value and the total measuring time was 7 h. Gaussian line broadening (5 Hz and 4 Hz) was used in the  $t_1$  and  $t_2$  dimensions, respectively. Only resonances with their sign opposite to the diagonal resonances are displayed. The ortho protons of the aromatic ring attached to C-1 and C-2 are labeled O1 and O2, respectively.

Inspection of the structures for the 11 possible photoadducts shows that only those for **2** and **3** lack a center, axis, or plane of symmetry which render the four cyclobutane protons and two carbomethoxy groups nonequivalent.



Further structural information was obtained from a COSY experiment recorded and processed to emphasize cross peaks arising from long-range (smaller) couplings<sup>4</sup> (included as supplementary material). Cross peaks were observed from couplings between H-1 and the doublet arising from aromatic ortho protons centered at 7.49 ppm in one ring and between H-2 and the doublet at 7.40 ppm, the second group of ortho aromatic protons. These results show that the aromatic rings were attached to C-1 and C-2, i.e., the photoproduct formed from head-to-head coupling

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(4) Bax, A. *Two-Dimensional Nuclear Magnetic Resonance*; Reidel: Boston, 1982; p 85.

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of methyl *p*-nitrocinnamate monomers.

Information from the standard spectrum and the COSY experiments do not establish the stereochemistry of the substituents because vicinal cyclobutane protons have similar *cis* and *trans* couplings.<sup>3</sup> However, it is possible to assign the stereochemistry of the photoproduct from a NOESY spectrum, Figure 1, which shows interactions between H-2, H-3, and H-4. As such interactions only occur when protons are spatially close, the protons must be *cis*; the absence of interaction between these protons and H-1 indicates that the latter is on the other side of the cyclobutane, i.e., structure 3 is correct.

The structural and stereochemical assignment is buttressed by ancillary observations from the NOESY spectrum. The doublet at 7.49 ppm, the ortho protons of the aromatic group attached to C-1 (O<sub>1</sub> in Figure 1), shows polarization transfer to H-1, H-2, and H-4; the first of these is the result of a geminal interaction, while the others are vicinal (*cis*) interactions. Similarly, the doublet at 7.40 ppm, the ortho protons of the aromatic group attached to C-2 (O<sub>2</sub> in Figure 1), shows a geminal interaction with H-2 and a vicinal (*cis*) interaction with H-1. These observations show the aromatic rings to be *trans* to each other on the cyclobutane. The second COSY experiment, recorded to emphasize cross peaks arising from long-range couplings, showed a weak cross peak between the proton on C-4 and

the low field *O*-methyl group. This peak indicates that the latter group is part of the carbomethoxy group attached to C-4. The higher field *O*-methyl group is therefore part of the carbomethoxy group on C-3. The upfield shift of this latter methyl group is probably caused by ring current shielding effects due to its position above the aromatic group at C-2.

The reassignment of the reported mixture as another head-to-head dimer of 1 shows that the regiochemical preference for this reaction path is greater than previously thought. There is no evidence of head-to-tail dimer formation.

### Experimental Section

A solution of 1 in benzene was irradiated as described by Ishigami et al. and the mixture separated by column chromatography on silica gel. The observed chemical shifts and splitting patterns of the isolated photoproducts were in good agreement with values reported previously.<sup>1</sup>

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**Supplementary Material Available:** COSY spectrum of 3 (Figure 1) that shows coupling between cyclobutane protons and second COSY spectrum (Figure 2) optimized for detecting long-range couplings between ortho aromatic protons and H-1 and H-2 cyclobutane protons (4 pages). Ordering information is given on any current masthead page.